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## K-XANES OF HIGHLY IONIC MATERIALS

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### ABSTRACT

X-Ray absorption spectra of Na K-edge in NaCl and NaF crystalline compounds are calculated according to the Full Multiple Scattering (FMS) approach in the framework of the one particle approximation. A 7-shell cluster of 93 atoms has been utilized for the calculation and good agreement with experimental spectra has been achieved.

### INTRODUCTION

Alkaly halides among the simplest crystalline systems are certainly one of the most used test for solid state theories and for experimental techniques. X-ray absorption spectra at the sodium K-edge are now available with high resolution ( $\Delta E \sim 0.5$  eV). [1] The spectra show strong differences in the edge region going from NaF to other sodium halides with the same crystalline structure.

Due to the little interstitial charge the lifetime of the electron in these systems is very large and as a consequence a great number of shells are necessary to make the calculation convergent. Moreover the strong ionic nature forces us to face the complex problem of a strong core hole interaction which is nearly absent in metallic and semimetallic materials where the hole is almost completely screened by conduction electrons. This effect is probably the cause of the excitonic lines present in all the spectra which are not well reproduced by our calculation.

### THEORY AND DISCUSSION

The many body problem for the photoexcitation of a core electron in a solid can be reduced to an effective one-particle Schrödinger equation known as Dyson equation

$$(\nabla^2 + E - V_c(\vec{r})) G(\vec{r}, \vec{r}'; E) - \int d^3r'' \Sigma(\vec{r}, \vec{r}''; E) G(\vec{r}'', \vec{r}'; E) = \delta(\vec{r} - \vec{r}')$$

where  $V_c$  is the usual coulombic or Hartree potential and  $\Sigma(\vec{r}, \vec{r}'; E)$  is an energy dependent complex and in general non-local exchange and correlation potential.  $G(\vec{r}, \vec{r}'; E)$  plays the role of propagator of the excited electron from site  $\vec{r}$  to  $\vec{r}'$  in the presence of the core hole. The photoabsorption cross section is:

$$\sigma(\omega) = -4\pi\alpha_0\omega \int d^3r d^3r' \phi_c(\vec{r}) \hat{\epsilon} \cdot \vec{r} \{ \text{Im} G(\vec{r}, \vec{r}'; \omega + E_i) \} \hat{\epsilon} \cdot \vec{r}' \phi_c(\vec{r}')$$

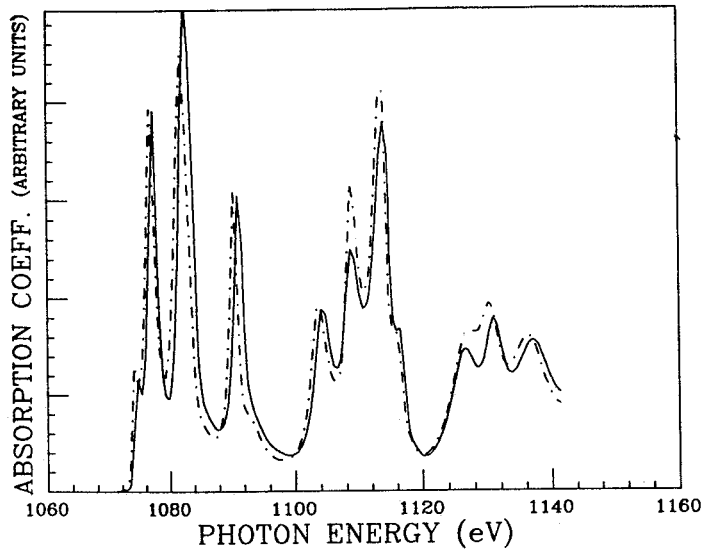


FIG.1 Theoretical  $X_{\alpha}$  Na K edge spectra for the NaF compound built by neutral wavefunction; the radii are obtained by Norman criterion: continuous line is for zero overlap, dotdash for 10% overlap. The spectra are undamped.

where  $\phi_c(\vec{r})$  is the photoelectron wavefunction in the initial core state with energy  $E_i$ ,  $\omega$  the photon energy and  $\alpha_0$  the fine structure constant.

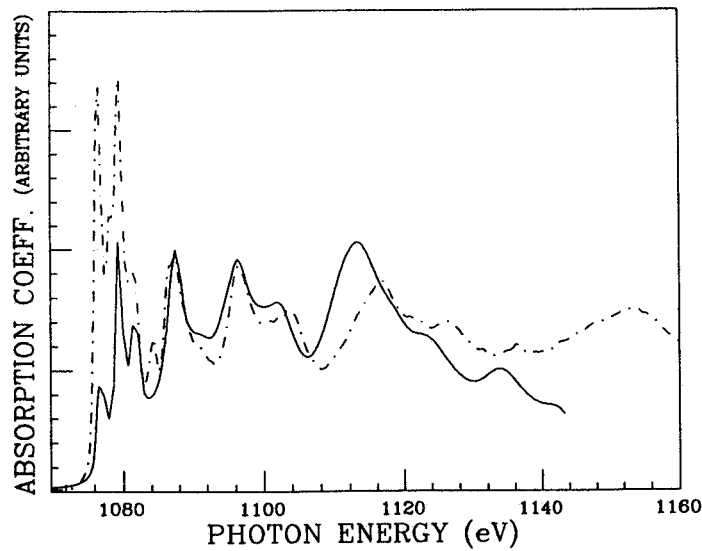


FIG.2 Na K edge for the NaCl. Experimental (dotdash) vs. theory (full line) according to the Pauling prescription for the ionic radii in the  $X_{\alpha}$  potential approximation.

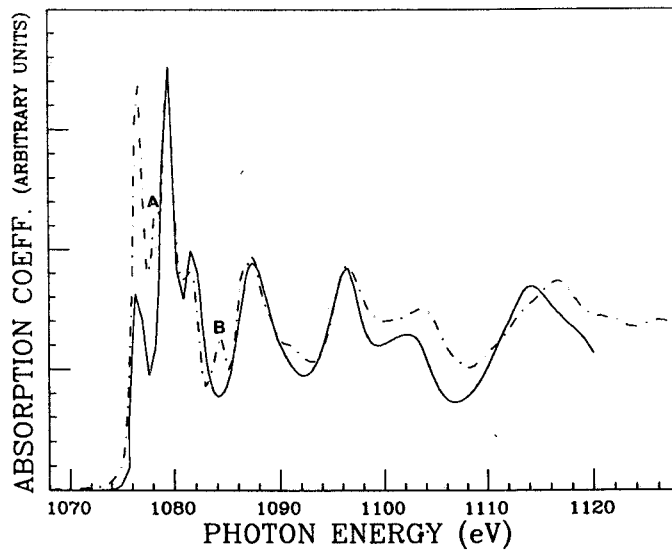
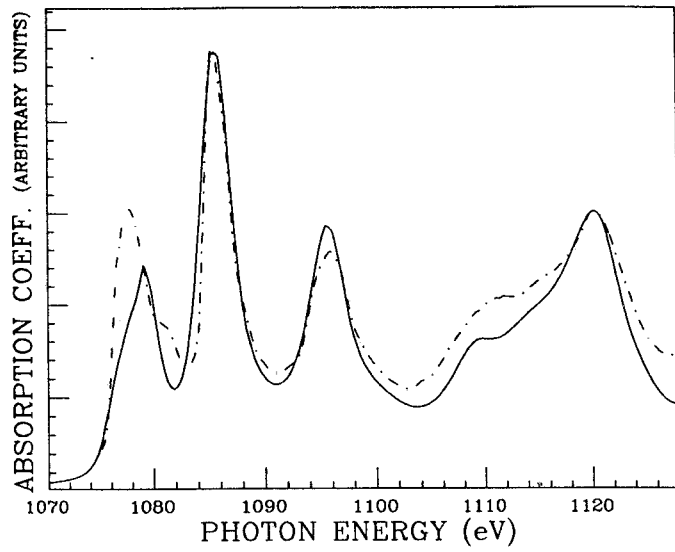


FIG.3 NaF(top) and NaCl (bottom) calculations vs. experiments (dotdash) from ionic charge density and a DH potential. The spectra are smeared to take account of the core hole term and experimental resolution.

In the FMS approach the conjugated Dyson equation can be solved imposing the correct boundary condition for the "incoming" electron only if one gives a local approximation for the self energy. For the problem under study one generally chooses between three different approaches:

a)  $X_{\alpha}$  energy independent exchange, [2] b) Dirac-Hara (DH) energy dependent exchange, [3] c) Hedin-Lundqvist (HL) energy dependent exchange and correlation. [4] The last is a complex potential which take account of inelastic channels for the photoelectron final state. (for a discussion see [5]) However also for the DH calculation we have used the imaginary part of HL potential in order to have a complex one. The total potential has been built using charge density from Clementi and Roetti ionic or neutral atomic wavefunctions, [6] then only the spherical contribution to the electrostatic potential has been retained. For the excited state we used the usual  $Z+1$  approximation or screened hole.

The muffin-tin radii are determined by the so called Norman criterion, [7] overlapping or not. As we can see in Fig.1 which shows two  $X_{\alpha}$  calculations of NaF spectrum by neutral wavefunction and a zero or 10% superposition of Norman radii, the differences regarding only the relative intensity of peaks are very little. Other possibilities include the choice of the radii using a matching potential criteria where the value determined for the first pair of neighbours has been extended to all other shells, both for the ground and the excited state potentials. Alternatively the ionic Pauling radii have been also used. [8] In Fig.2 we present a comparison with experiment of NaCl spectrum built from a  $X_{\alpha}$  calculation from ionic wavefunctions and ionic muffin-tin radii. Even in this case we observe only a mismatch in the edge region for the relative intensities. Best results are however obtained from superposition of ionic spheres with zero overlap and using a Dirac-Hara exchange potential. In effect there are little differences between the results with a HL or with a DH potential, however the latter one gives better peaks position. For NaF the agreement is surprising while for NaCl, although the shape well matches the data, at higher energies the calculated spectra is a slightly contracted. Fig. 3 shows these final DH calculations for NaF and NaCl respectively convoluted with a lorentzian function whose width represents the core-hole term and the experimental resolution.

Work is in progress to calculate other alkaly halides spectra and to improve the agreement with experimental results. Particular attention is devoted to the investigation of features A and B in the NaCl spectrum reported in Fig.4. [9]

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## REFERENCES

- [1] T. Murata, T. Matsukawa and S. Naoe', Solid State Commun. 66, 787 (1988) and private communic.
- [2] J.C. Slater, *The Self-Consistent Field for Molecules and Solids; Quantum Theory of Molecules and Solids* (McGraw-Hill, New York 1979).
- [3] S. Hara, J. Phys. Soc. Japan 22, 710 (1967).
- [4] L. Hedin and B. Lundqvist, J. Phys. C: Solid State Phys. 4, 2064 (1971).
- [5] S.H. Chou, J.J. Rehr, E.A. Stern and E.R. Davidson, Phys. Rev. B35, 2604 (1987).
- [6] E. Clementi and C. Roetti, *Atomic Data and Nuclear Data Tables*, 14, 177 (1974).
- [7] J. Norman, J. Chem. Phys. 61, 4630 (1974).
- [8] L. Pauling, *The Nature of Chemical Bond*, (Cornell University press,1967).
- [9] R. Gunnella, M. Benfatto, A. Marcelli, C.R. Natoli, T. Murata, T. Matsukawa and S. Naoe', to be published.